DIRECT IODINATION OF ORGANIC COMPOUNDS THRU THE AGENCY OF NITRIC ACID

and

DETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS BY THE MEANS OF LIQUID AMMONIA.

By

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Department of Chemistry.

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Part I.

Part II.

DIRECT IODINATION OF ORGANIC COMPOUNDS THRU THE AGENCY OF NITRIC ACID.

The portion of this work which concerns iodination thru the agency of nitric acid was suggested by the work done on this subject by Messrs. Rasik Lal Datta and Nihar Ranjan Chatterjee in the laboratories at Presidency College, Calcutta, India.[1]

The direct introduction of iodine into organic compounds has received the attention of various investigators. Altho Iodine in its general characteristics is similar to Cl and Br, yet is does not like these, except in the case of Basic compounds of the type $C_6H_5.NH_2$, produce direct substitution products with organic compounds. The reason for this may be sought in the fact that the by the substitution formed HI causes the derivatives to break down, or, in fact, their genesis is in general prevented. A separate oxidizing agent must then be added to clear the way for the iodine. Kekulé[2] first used Iodic acid for this purpose. Hlasiwetz and Weselsky[3] used HgO in the following

[1] J.A.C.S. -39, 435 (1917)

[2] C. 1870 -63

[3] Ann. 131, -128.

manner;

$$3C_6H_5OH + HgO + 2I_2 \text{ (alcoholic sol.)} \quad -- \quad 3C_6H_4.I.OH + HgI_2 + 2H_2O$$

Lothar Meyer used Ferric Cloride;[1]

$$3C_6H_6 + 3I_2 + FeCl_3 \quad -- \quad 3C_6H_5.I + 3HCl + FeI_2 + I$$

Hofmann[2] used yellow phosphorus, and Beilstein[3] the red; $3CH_3CH_2OH + P + I_3 \quad -- \quad 3CH_3CH_2I + PO_3H_3$, while Lal Datta[4] also mentions a modified method for the use of phosphorus in the preparation of C_3H_5I. Potassium persulfate and sulfur iodide were also used by Lal Datta.

There seems to be no recorded instance of the use of nitric acid for this purpose previous to that of Messrs. Chatterjee and Lal Datta. They have by this method successfully made derivatives of benzene, toluene, Xylene, cymene, mesitylene, hexane, thiophene, ethyl benzene, naphthalene and anthracene. The specific conditions of temperature, etc., under which each of these was prepared have not been described, but the general method was that of mixing the iodine and the substance to be iodinated, heating to a desirable temperature and then adding nitric acid in small portions of about 2 c.c. until the reaction

[1] Ann. 231, -195

[2] Ann. 126, -250

[3] Ann. 115, -273

[4] J.A.C.S. 36, - 1005

with the iodine present was completed. The iodine enters directly, and they have assumed that the nitric acid does not merely play the part of a catalyst, but actually atkes part in the reaction, being reduced to the lower oxides of nitrogen,- the hydrogen of the ring being oxidized and the iodine taking the place thus rendered free. They have further found that the method is not applicable where the chances for nitration are greater than the chances for iodination, and that in case the nitric acid is of too great concentration, hydrolysis takes place with the formation of phenols. The latter was especially true of the aliphatic halides, but the aromatic halides are less easily hydrolysed and consequently not so sensitive to the concentration of nitric acid used.

The experimental work which follows was undertaken to learn the possible effects upon the entry of iodine into the ring of the presence of other groups of atoms in the benzene ring. The method used was intended to follow that described above, but in each case the concentration of acid used, temperature to be maintained, etc., had to be chosen to suit the substance being treated. The amount of acid to be used was determined by the progress of the reaction, fresh portions being added as it was noted that the reaction with the last portion was complete, or nearly so.

In most cases the progress of the reaction was quite readily followed by the amount of uncombined iodine which made its appearance in the condenser tube, and by the general appearance of the reaction product.

The apparatus used was especially arranged for the experiments. A long, narrow-necked oxygen flask was the container used. Into the narrow neck was ground the end of a glass condenser-tube so as to fit snugly and yet be easily removed. In this manner the use of corks, which at best would last only a few minutes, was avoided. A long glass rod was found very satisfactory for pushing down into the container any iodine which might sublime and attach itself to the walls of the condenser-tube.

It is not assumed that this investigation is complete in its detail. In many cases complete identification of the products formed has not been possible within the time assigned for this work. It is also possible that in some cases, fresh trials under different conditions as to concentration of acid, temperature, etc., might give entirely different results.

On the pages immediately following will be found a tabulated summary of the compounds treated, the products obtained, etc., together with other facts.

Halogen determination made upon the products are not written up in detail with the experiments. They will be found so given in the other part of this work dealing with Halogen Determinations by the Liquid Ammonia Method.

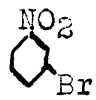
Substance Treated.	Products Formed.	Temp. used.	Melting point. Obs.	Melting point. given.
$C_6H_5.Br$	(1)Br(4)I.C_6H_4	150 - 160	89-90.5	92
$C_6H_5.Cl$	(1)Cl(4)I.C_6H_4	160- 165	54-56	56
	(1)Cl(2)I.C_6H_4 or (1)Cl(3)I.C_6H_4	"		
$C_6H_5.I$	(1)I(4)NO_2.C_6H_4	165- 190	165 - 170	171
$C_6H_4.Br_2$ (p)	The same recovered	180 - 190	77 - 89	89
$C_6H_5.NO_2$	The same recovered	125 - 175		
$C_6H_5.COOH$	(1)COOH(3)I.. C_6H_4	135- 140	183 - 184.5	186
C_6H_6	$C_6H_5.I$	120 - 130		
	(1)I(4)I.C_6H_4 (?	"	127- 130	129.4
	Picric Acid	"	121- 122	122.5
$C_6H_5.OCH_3$	(1)OCH_3(4)I. C_6H_4	150 - 160	51- 52	52
$C_6H_5.NHCOCH_3$	 (Thot to be this)	112	130	159
	(1)$NHCOCH_3$(4)I. C_6H_4	Ice- bath	185- 188	199
Anisidine	The 2-3 di- nitro anisidine	Below Room	214- 217	220
Phenacetin	The 2-3 di- Nitro phenacetin	Ice- bath	205- 206	206
C_6H_4(1)CH_3. (4)Cl	C_6H_4(1)COOH. (4)Cl	110- 150	220 - 231	236
C_6H_4(1)CH_3 (3)Cl	C_6H_3.(1)CH_3 (3)Cl (?) I	140- 180		
"	(?)	"	115- 130	
C_6H_4.(1)CH_3 (2)Cl	C_6H_3.(1)CH_3 (2)Cl (3)I (?)	170 - 180	72- 74	none
	(?)	"		
	C_6H_3.(1)CH_3 (2)Cl (4)NO_2	"	65- 67	65-68

Boiling point Obs.	Boiling point Given	Yield (Pure) Gms	Yield (Pure) P/ct.	Iodine Content Found	Iodine Content Theoret.	Remarks
				44.67		
		22	40	45.85	44.85	
				52.85		
		21.5	58	52.95	53.20	
220-225	234 at 760MM Mercry	11.	30	52.80	53.20	
				53.00		
				51.05		
				49.85	50.98	
				None		
200-208	205			None		
				51.23		
		10	53	51.01	51.19	
183-186	186	17.3	54	Present		
		Neg.		Present		
		.5 - 1.		None		
		8 - 9		53.62	54.25	
		Neg.		70.53	70.00 (?)	
				69.99		
		1.5-5. cr	20-40	48.60		
				48.38	48.83	
		Heavy		None		
		Heavy		None		
				None		
241-243	242-243	18.5	64	49.60	50.20	
				49.40		
		Neg.		Test		
215 - 220 at 52MM	None	2 g.		50.86		
				50.21	50.20	
174 at 52mm.		4 -5 not known		Present		
				None		

B R O M - B E N Z E N E .

A first trial was made with 5 c.c. brom-benzene and 5 gms. iodine heated on a water-bath for about 2 1/2 hours. During this time nitric acid of sp. gr. 1.4 was added in small portions of 1 - 2 c.c. until about 15 c.c. had been used. No results were obtained. A similar mixture was then boiled over an electric hot-plate. A reaction ~~then~~ took place with the formation of oxides of nitrogen. The iodine present gradually disappeared, the deep red color giving way to a delicate pink. Upon cooling, a solid precipitated ~~with~~ which was soluble in hot alcohol. After two recrystallizations, lustrous plate crystals melting at 88°.5 - 90° were obtained.

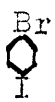
The experiment was repeated with 20 gms. iodine and 18 c.c. brom-benzene heated over an oil-bath at 150° - 160°. As before, nitric acid was added in small portions as rapidly as it was used by the reaction. The total amount added was 21 c.c. The reaction was complete after 5 1/2 hours, the color of iodine having almost entirely disappeared. The solid formed was washed with dilute alkali, with water and then with dilute sodium thiosulfate to remove any still remaining free iodine. When recrystallized from alcohol the lustrous plate crystals melted at 89° - 90°.5 .

By Kjeldahl determination these contained no nitrogen, hence the product could not be I 

which, according to Richter, melts at 90°.

Halogen determination made by the liquid ammonia method gave the following results;

	No. I.	No. II.
Percent iodine	44.67	45.85



melts at 92° and has a theoretcial iodine content of 44.85 percent.

The yield of recrystallized (1) brom - (4) iod - benzene was twenty grams. This is 38 percent of the theoretical, based on the amount of iodine used.

No other iodine-containing products were identified.

C H L O R - B E N Z E N E .

30 grams of iodine and 18 c.c. of chlor-benzene were used. The temperature was at first kept near 130° but the reaction at this temperature being slow, it was raised to 160°-165° where is was maintained for seven hours until most of the iodine had been acted upon, which was determined by the lighter color of the mixture. During this time 24 c.c. of nitric acid (sp. gr. 1.4.) had been added in 2 c.c. portions at varying intervals.

The reaction product was a very viscous oily substance in which crystals of a solid were evident. Recrystallized from hot alcohol, lustrous plate crystals much similar to those obtained from brom-benzene were obtained. These melted at 54° - 56°. A quantitative determination of their halogen content by the liquid ammonia method gave the following results;

	No. I.	No. II.
Percent iodine found	52.85	52.95

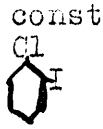
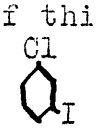
(1) chlor - (4) iod - benzene melts at 56° according to data given by Richter, and has a theoretical iodine content of 53.2 percent.

The yield of (1)chlor - (4) iodbenzene was 21.5 grams of recrystallized product, which is 58 percent. (Calculations based on amount of iodine used.)

When water was added to the alcoholic filtrate from which the crystals had been obtained, a reddish oil was immediately precipitated. This was steam-distilled and the oil which came over washed with thiosulfate and finally dried with calcium chloride. The dried oil was distilled. The boiling temperature rose rapidly to 220° , only about 3 c.c. being collected up to that point. The remainder came over at 220° - 225°. (Barometric pressure 730 MM.) During distillation the oil decomposed slightly with the liberation of iodine. It was again washed with sodium thiosulfate and the colorless oil dried over calcium chloride.

Halogen determination made by the liquid ammonia method resulted as follows;

	No. I.	No. II.
Percent Iodine found	52.80	53.00

There are two apparent possibilities for the constitution of this product. It might be either  or  , in both of which the theoretical iodine percentage is 53.20. The first is described as a colorless oil boiling at 234° - 235° , (Barometric pressure 760 mm.), the latter at 230° (Barometric pressure not given). Attempts to distinguish them by oxidation are described on page 39 .

The yield of this redistilled oil was 11 gms. or 30 percent, based on the amount of iodine used. It will be noted that in this reaction 88 percent of the reacting substances were accounted for as purified products.

I O D - B E N Z E N E .

An attempt to add a second iodine to the ring in iod-benzene was made as follows;

17 grams iod-benzene and 25 grams iodine were heated together on the oil-bath while 2 c.c. portions of nitric acid (sp. gr. 1.4) were added at 15 - 20 minute intervals. The temperature was at first kept at 165° but since no reaction with the iodine was apparent, it was soon raised to about 190°. After 5 hours and 50 minutes continued heating the iodine still appeared intact and the process was discontinued. The resulting product was a dark semi-solid which when steam-distilled gave up large quantities of unchanged iodine. None of the product came over with steam.

Repeated recrystallization from benzene yielded a white product melting at 165°- 170° which gave a qualitative test for nitrogen. Halogen determinations made by the liquid ammonia method gave the following results;

	No. I.	No. II.
Percent iodine found	51.05	49.85

melts at 171° and has a theoretical iodine content of 50.98 percent.

A second attempt was later made with results apparently identical to those recorded above.

(P) - D I -B R O M B E N Z E N E.

Having found it possible to introduce an iodine into the ring when one place is already occupied by a chlorine or bromine, but from the observations on page 15, apparently not possible to introduce a second iodine directly, an attempt was made to add iodine to the ring when already containing two atoms of ai different halogen.

17 grams of p-di-brombenzene and 10 grams of iodine were heated at 150° over an oil-bath, nitric acid of sp. gr. 1.4 being added as in former experiments. The heating was continued for over three hours at this temperature with no apparent reaction resulting. The temperature was then run up to 180°- 190° with no better results. The iodine was driven off into the condenser tube, the amount recovered being about 8 grams.

Upon cooling, a solid was left in the bottom of the flask. This when recrystallized from alcohol melted at 75°- 81° . Nothing of better melting point was obtained. No ########## ##### ## iodine was indicated by qualitative tests and it was finally concluded that the result was a mixture of the di-brom benzene together with some nitro products.

N I T R O - B E N Z E N E .

10 c.c. of nitro-benzene and 10 grams of iodine were heated on an oil bath at temperatures varying between 135° and 175° for almost six hours, while nitric acid of sp. gr. 1.4, was added in 2 c.c. portions. 35 c.c. of nitric acid were used. No reaction with the iodine was apparent and practically all of it was recovered in the tube of the condenser.

An oil was left in the bottom of the flask from which the iodine was washed with sodium thiosulfate. It was then steam-distilled and, after drying with calcium chlorided, boiled at 200°-208° . By test no iodine was present. Nitrobenzene boils at 205° . The recovery of nitrobenzene amounted to about 6 c.c.

Small traces of a water soluble product were observed which yielded no qualitative test for iodine. It is likely that this was some of the di-nitro product.

It is possible that the temperatures used were not high enough to obtain results, but the above would seem to indicate that where one place in the ring is already occupied by a nitro group, iodine cannot be added thru the agency of nitric acid.

B E N Z O I C A C I D .

Twelve grams of benzoic acid (m.p. 121°) were heated over an oil-bath with ten grams of iodine. The temperature was at first raised to slightly above the melting point and kept at 135° - 140°. When nitric acid (sp. gr. 1.4) was added in small portions of 2 - 4 c.c. at intervals of 10 - 20 minutes, a ready reaction resulted. With continued heating the iodine was gradually acted upon, but at the end of three hours much of it still remained intact. The temperature was then raised to about 170° for a few minutes to drive off any excess iodine, which ~~might be~~ was collected in the condenser tube. A white, lumpy solid was left in the bottom of the flask, from which the water and excess acid were poured while still hot. The lumpy solid was further treated with boiling water to remove any more soluble portions of unchanged benzoic acid. The remaining solid was recrystallized from alcohol twice, when a white, crystallin e compound (flaky crystals) melting at 183° - 184.5° was obtained. This was soluble in dilute alkali and quantitative determinations made upon it for iodine by the liquid ammonia method gave the following results;

	No. I.	No.II.
Percent iodine found	51.23	51.01

This would indicate 

, melting point 186°, (Richter) and theoretical iodine content 51.19 percent.

The yield of purified product was about 8 grams, or about 41 percent of a theoretical 19.2 grams. Both unchanged ### iodine and benzoic acid were recovered. Hence it might be possible to increase the percent yield by using a higher temperature or prolonging the period of heating.

B E N Z E N E .

This experiment was carried out for the express purpose of learning if the methods used in the previous experiments would yield results similar to those obtained by Messrs. Lal Datta and Chatterjee. (J.A.C.S. March, 1917) They mention having used benzene in the preparation of mono-iodbenzene.

30 c.c. benzene and 23 grams iodine were heated on an oil-bath regulated at 85° while small portions of nitric acid (1 - 2 c.c.) were added. Oxides of nitrogen were freely given off. The reaction being slow at 85° , the temperature was raised to 120° - 130° and maintained there for 2 hrs. and 40 minutes. When it was thot that the reaction was fairly complete, the temperature was raised to 175° to drive off into the condenser-tube any excess iodine. The total time of heating was 3 hrs. and 30 minutes.

The reaction product was steam-distilled. Iod-benzene came over as a reddish oil. This was washed with sodium thiosulfate to remove free iodine, dried with calcium chloride and distilled. The portion boiling at 183°-186° was caught. Iod-benzene boils at 186°. The yield was 17.3 gms., or 54 percent.

Lal Datta and Chatterjee mention yields as varying between 60 and 70 percent.

A residue remained after the distillation of the iod-benzene. This when recrystallized from alcohol, melted at 127° - 130°. Not enough of this product was obtained for successful analysis, but since the gentlemen above referred to having obtained small yields of  , (M.P. 129) it was assumed that this product was the same. It should be noted that no such product was detected among the products resulting from the attempt to introduce another iodine into the ring in iod-benzene as described on page 15. It must be assumed that the presence of an excess of benzene prevents to some extent the oxidation of this second iodine and thus small portions of the di-iodbenzene are permitted to form.

The residue remaining in the steam-distillation flask was concentrated and from this solution a yellow crystalline product was separated. This proved to be picric acid, melting at 121° - 122°. The recrystallized yield was about .5 gm. This had also been obtained by the gentlemen at Calcutta.

A N I S O L E . $C^6H^5.OCH^3$ B.P. 155°.

12 c.c. anisole and 10 gms. iodine were heated together on an oil-bath at 150° - 160°. The reaction, when nitric acid (sp.gr. 1.4) was added in 2 c.c. portions, was quite rapid. The first 10 grams of iodine had been reacted upon within 20 minutes and 4 more were added to make up the 14 grams theoretically necessary. The last reaction was complete within 10 minutes. In all, 13 c.c. of acid were used.

The resulting product was a red oil, the color not being removed by thiosulfate. After drying with calcium chloride, it was distilled. Boiling began at 220°. A first portion was caught between 220° - 240°, a second at 240° - 250° and the remainder at 250° - 270°. Upon standing a few minutes all three portions became solid. Recrystallization of each yielded a pink crystalline solid melting at 51° - 52°. The percent iodine was found by the liquid-ammonia method to be 53. 62.

melts at 51° - 52° and boils at 237° under 726 mm. pressure. It theoretical iodine content is 54.25 percent.

The solidified portion after distillation amounted to 13 - 14 gms. The recrystallized yield was 8 - 9 gms., or nearly 40 percent.

A C E T A N I L I D E .

For a first trial, 15 grams of acetanilide and 15 grams iodine were heated over the oil-bath at about 135° . When nitric acid was added a very rapid reaction took place. The heating was continued for twenty mintues during which time 11 c.c. of the acid were added. But upon examination the product was found to be charred beyond any possibility of purification and it was abandoned.

A second attempt was made with the temperature maintained just at the melting point of acetanilide, 112° . The reaction went on as before. Heating was discontinued after about one hour. The product formed was a solid, still somewhat charred. This was steam-distilled when, after the remaining free iodine had come over, a black solid was carried over which after being recrystallized from alcohol, melted at 130° . These crystals were flaky and slightly pink, which color repeated recrystallization failed to remove. Halogen determinations made on the product gave the following results;

	No. I.	No.II.
Percent Iodine found	70.53	69.99

This does not correspond either in melting point or iodine content to any of the iod-acetanilide products which might be formedand, since the

supply of material was limited, no other determinations could be made.

The residue in the flask after steam-distillation proved to be a black tarry mass from which no crystals could be obtained by any of the ordinary solvents. It was finally abandoned.

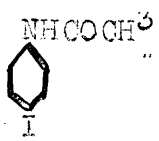
A third attempt was made with the same materials, but in this case the iodine and acetanilide were first intimately mixed by fusing at a temperature slightly above the melting point of acetanilide. The mixture was then cooled to slightly above room temperature and the nitric acid added in small portions with continued shaking. The reaction went only slowly at first, but as more nitric acid was added, it became more rapid until, finally, in spite of a cooling water-bath a greal amount of heat was generated and the entire mass was charred. From this a very small amount of a product melting at 120° was obtained, but not enough to determine whether or not it was the meta-iod-acetanilide, which, according to Richter, melts at 119°.5 .

For a fourth trial the ingredients were ground together and cooled with an ice-bath. The nitric acid, (diluted to two parts acid sp.gr. 1.4 to one part water) was added in very small quantities. In this manner the reaction was controlled, but

toward the last much heat was developed, tho the product did not char as before. The excess iodine was removed by thiosulfate and the recrystallized (from alcohol) product melted at 183° - 184°. This was a sandy substance with a slight red color which was not removed by any of the common methods. It gave tests for iodine, and halogen determinations made by the liquid-ammonia method gave the following results;

	No. I.	No.II.
Percent Iodine found	48.60	48.38

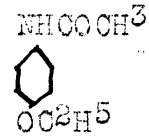
This was evidently the para-iod-acetanilide,



, which is mentioned by Richter as melting at 183° and has a theoretical iodine content of 48.83 percent.

The amount of the crude substance was about 5 grams (recrystallized , 1.5 grams) as against 10.2 grams theoretical. Some unchanged acetanilide was recovered and a considerable amount of unused iodine was removed by the first washing with thiosulfate.

P H E N A C E T I N .



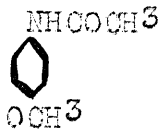
Because of the ease with which phenacetin is reacted upon by nitric acid, the following experiment was carried out in an ice-bath.

14 grams of phenacetin and 10 grams iodine were shaken and cooled continuously while small protions of acid (sp. gr. 1.4.) were added. The controlled reaction went on readily and was considered complete at the end of one hour, when 35 c.c. of acid had benn added. A very light, flaky, yellow product was formed which remained suspended in water. Iodine removed and recrystallized from alcohol, the crystals obtained melted at 205° - 206° and gave no test for iodine.

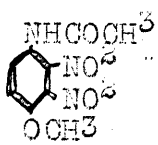
is recorded by Richter as melting at 206°.

The yield of this substance was quite heavy. No other products were obtained. Attempts were later made to iodinate this product at temperatures mounting to 195° and continued heating, but no reaction was obtained with the iodine.

A N I S I D I N E .

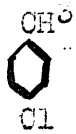


Anisidine, like phenacetin, reacted readily with the nitric acid at room temperature and below. The same plan was followed as with phenacetin. A yellow, sandy appearning precipitate was formed which, when recrystallized from alcohol, melted at 214° - 217° . It gave no test for iodine, practically all the iodine used being recovered.



melts at 220°.

PARA - CHLOR - TOLUENE



Ten grams of the toluene and ten grams iodine were heated over an oil-bath at a temperature of 110° - 125° for three hours while nitric acid in 2 c.c. portions was added from time to time. A reaction immediately took place with the liberation of the oxides of nitrogen, but no visble effect on the iodine was noted. The temperature was then raised to about 180° and maintained there. In the meantime at white solid had been formed from which the excess acid was drained. This was somewhat soluble in water and portions were recrystallized from that solvent, yielding a product melting at 200° - 221°. The whole was very soluble in dilute alkali and was reprecipitated from this solution when made acid. Qualitative tests showed no iodine present in the product. Para-chlor-benzoic acid melts at 236°, and it was concluded that oxidation of the methyl group had taken place, with the possible formation of some nitro product which was difficultly separable from the acid. The larger part of the iodine used was recovered.

In order to confirm the above, a second experiment was carried out at higher temperatures, 140° - 150°. The same white product was formed from which

a more insoluble portion was separated, melting at 230°- 231°. Iodine was recovered.

From these results it may be assumed that in case the para position of a toluene is already filled by a chlorine group, iodine cannot be made to enter the ring thru the agency of nitric acid.

META - CHLOR - TOLUENE

For a first trial ten c.c. of m-chlor-toluene and ten grams iodine were used. The temperature was kept at 140° while nitric acid (sp. gr. 1.4) was added in small portions of 2 - 3 c.c. during a period of 4 hours. A reaction continued thruout with the evolution of oxides of nitrogen. When practically all the iodine had been reacted upon, the temperature was raised to 180° for a few minutes to drive off any excess iodine.

The oil formed during the reaction was separated from the water and acid by decantation, and then washed with fresh portions of boiling water to remove any water soluble products formed, and later with dilute sodium thiosulfate to remove free iodine. It boiled at 230° - 250° when distilled, was a colorless oil, insoluble in dilute alkali and water, and without further purifiaction gave the following quantitative results for halogen by the liquid-ammonia method;

No's.	I.	II.	III.	IV.
Percent iodine	41.6	39.3	47.4	38.3

The product, evidently not pure, was redistilled, the larger portion boiling at 240° - 241° being taken for a second anlysis which resulted as follows;

	No. I.	No. II.
Percent iodine	47.07	47.40

This oil agreed in boiling point and physical properties with the chlor-iod-toluenes recorded by Richter as boiling at 240° - 242°. No reason can be assigned for the low percentage of halogen, which should be 50.30 percent, unless the process of determination was at fault.

Assuming the product to be a meta-chlor-iod-toluene, the total yield of 12 grams would be 61 percent of theoretcial, as based on the amount of iodine used.

Besides the above, a small portion of a water soluble substance (white and crystalline) was recovered. This gave no test for iodine. It melted at 115°- 130°.

The whole process was repeated with slight variations. 15 grams each of iodine and m-chlor-toluene were treated with nitric acid as above at 175°- 180°. At this temperature the reaction required two hours and thirty minutes for completion. The oil was steam-distilled, washed with thiosulfate, and then again steam-distilled, washed and dried. The dried oil distilled over at 238°- 248°, the larger portion coming over at 241°- 243°. The yield was 18.5 grams or 64 percent, which was practically the same as before, perhaps increased by better manipulation.

Quantitative analyses by the liquid-ammonia method gave the following results;

	No. I.	No. II.
Percent iodine	49.60	49.40

This is still somewhat below the theoretical, $$$$ 50.20 percent, but near enough to establish the identity of the product as a meta-chlor-iod-toluene. A discussion of its exact constitution is to be found at another place in this work under a note concerning the constitution and properties of some chlor-iod-toluenes.

The above work would indicate that when the meta position of a toluene is filled by a chlorine atom, iodine readily enters into the ring thru the agency of nitric acid.

ORTHO - CHLOR - TOLUENE

The ortho-chlor-toluene for use in this experiment was first prepared from ortho-toluidine by the ususal method of diazitization and cuprous chloride.

Twelve grams of this and ten grams iodine were heated on an oil-bath at 120° while nitric acid (sp. gr. 1.4) was added in 2 c.c. portions at 10 - 20 minute intervals. A reaction took place with the liberation of oxides of nitrogen, but none of the iodine seemed to take part in the reaction. The temperature was then raised to 160°- 165° for a period of 6 hours, at the end of which time all but a very little of the iodine had been reacted upon.

A dark oil was formed in the bottom of the flask from which the aqueous layer was poured. It was then washed with water to remove any water soluble products. From this wash water a white crystalline product was obtained which contained no iodine and melted at 65°- 67°. The yield was 1.5 grams.

is referred to be Richter as melting at 65°.5 - 68°.

The remaining oil was washed with sodium thiosulfate and then steam-distilled. The yellow oil which came over was only slightly volatile and several hours were required to obtain about 10 c.c. The distillation was discontinued and extraction with chloroform resorted to. These extractions were added to the portion already distilled, and the chloroform distilled off over a water-bath. When all the chloroform had been driven off and the temperature began to rise toward 100°, it was noted that the oil decomposed with the liberation of iodine. The heating was discontinued and apparatus was arranged for distillation at reduced pressures. At 30 millimeters of mercury and 135° the first drops appeared in the receiving vessel, ~~at 135°~~, but the temperature of the liquid rose rapidly to 195° and the bulk of the oil came over at 195°- 210°. It was very viscous and slightly decomposed. The distillation was repeated on the last portion at the same pressure, when it all came over at 195°- 205°. The yield was 4 - 5 c.c.

For purposes of further identification, the experiment was repeated with modifications. 40 gms. ortho-chlor-toluene and 40 gms. iodine were used, and the temperature maintained at 170°- 180° for 7 1/4 hours. 60 c.c. of nitric acid were used. (sp.gr. 1.4)

Steam-distillation was again ##### tried on the product, free iodine coming off first and then a yellow oil which, as noted above, was only slightly volatile. This was washed with dilute NaOH to remove any OH or COOH products. But since the oil was not easily carried over by steam, distillation was finally abandoned and the whole treated with dilute NaOH. It was then washed with hot water, which removed much of the solid. This proved to be para-nitro-ortho-chlor-toluene. It was then discovered that the oil ###### was quite insoluble in 90 percent alcohol, even when hot, and in this manner the remaining solids were readily removed.

The product at his stage was of a deep golden, yellow color. Quantitative determinations made for iodine by the liquid-ammonia method gave the following results;

	No. I.	No.II.
Percent iodine found	41.47	40.21

Theoretical, if a chlor-iod-toluene, 50.20 percent.

Distillation was carried out at about 52 mm. of mercury. The first drop came over at 155° and for a short time the temperature was steady at 174°, finally rising rapidly to 190°. At this point another portion was caught, the bulk of which boiled at 215° - 218°. A third portion boiled at 218° - 220°,

and the distillation was discontinued when the temperature mounted rapidly to 255°.

Of the three portions, only the first remained a liquid. The last solidified almost immediately in the condenser tube, while the second was solid after standing for a few minutes. Attempted halogen determination on the liquid showed it to be quite impure. The solid was also slightly decomposed, iodine having been liberated. This was removed with alcohol.

The solid material had a very low melting point (30°-35°) and seemed to impregnated with an oil. Halogen determinations resulted in;

	No. I.	No. II.
Percent iodine	48.94	47.35

Dry crystals of this product were only obtained after pwolonged standing on a porous plate in a dessicator. These were yellow in color and melted at 72°-74°. Halogen determinations resulted as follows;

	No. I.	No. II.
Percent Iodine found	50.86	50.21

Theoretical for chlor-iod-toluene, 50.30 percent.

The yield of purified product , 2 grams, considering the amount of iodine and toluene used, was exceedingly small. It is likely that upon re-

petition of the experiment this could be increased. No other products containing iodine were recovered, so much of it must have been lost by handling. About 10 grams of the 40 grams iodine used were recovered.

The exact constitution of this substance is a matter to be settled by future investigations. On the following pages will be found a short discussion of the possible chlor-iod-toluenes.

A NOTE CONCERNING SOME CHLOR-IOD-TOLUENES.

The following chlor-iod-toluenes are mentioned by Richter;

I	(2)chlor-(?)iod-toluene.....	B.P. 240°
II	(2)chlor-(3)iod-toluene.....	Fluid (yellow)
III	(2)chlor-(5)iod-toluene.....	B.P. 132°- 133° at 25 mm.
IV	(3) (?)chlor-(?)iod-toluene.....	B.P. 242°- 243°
V	(?)chlor-(?)iod-toluene.....	B.P. 240°

From meta-chlor-toluene was obtained an iod product which boiled at 241°- 243°(730 mm. mercury). This would indicate that in number IV of the above series the chlorine atom is really in the (3) position. The position of the iodine atom has not yet been ascertained.

From ortho-chlor-toluene was obtained a viscous yellow liquid which corresponded to the description of number II. Number II has been prepared by the decomposition of (2-4)dichlor-(3)iod-toluene at 88°.[1] (No boiling point is recorded.) But when the liquid obtained from ortho-chlor-toluene by the experimental method was distilled at 52 mm., the portion boiling at 215°- 220°proved to be a solid at room temperatures with a melting point at 72°- 74°when dry . (Cf. P. 36)

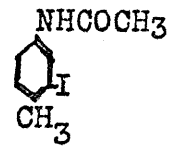
[1] Central Blatte , 1907 - (1) - 1198.

Halogen determinations showed it to be a pure chlor-iod-toluene. There can then be two conclusions concerning this product. Either it is not number II of the above series at all, but the other fourth possible ortho-chlor-iod-toluene (not mentioned above), or the product described by Richter contained small portions of other chlor-iod-toluenes which lowered its melting point to below room temperatures. The latter is ~~very~~ probably the case, since no attempt at distillation of the yellow fluid is recorded.

The exact nature of the liquid which was distilled off before the solid portions came over (See p. 35) was not determined. It was of a watery consistency and slightly yellow. Attempted halogen determinations showed it to be quite impure.

If the solid melting at 72° - 74° really is (2)chlor-(3)iod- toluene, it should oxidize to give a benzoic acid product melting at 210°. Pending investigation of a suitable method for the oxidation of chlor-iod-toluenes without removal of the iodine, further investigation of this product was postponed.

In connection with these attempts at oxidizing chlor-iod-toluenes, it might be said that a 10 percent solution of nitric acid proved too strong. The CH_3 group was oxidized to COOH but not without removal of the iodine. Another method used by Wheeler and Liddle

for the oxidation of such compounds as  was given one trial which did not prove successful. Lack of chlor-iod-toluenes in sufficiently large amounts prevented a second trial of this method being carried out. For purposes of future reference the method is briefly described as follows;

6 gms. of the oil and 250 c.c. of water were heated in a 2 liter flask by forcing in steam. To this 12 gms. of $MgSO_4$ were added and the heating continued. Thru the reflux a 1 percent solution of $KMnO_4$, containing 10.5 gms. $KMnO_4$ in 1050 c.c. of water, was added slowly at first and then more rapidly as the volume increased. The mixture was then heated with steam for 1 1/2 hour, after which sufficient alcohol was added to reduce all the $KMnO_4$ to MnO_2. After cooling the MnO_2 was filtered off and washed with water. The clear solution was evaporated and examined for the desired products.

DETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS BY THE MEANS OF LIQUID AMMONIA.

The use of the ionizing powers of liquid-ammonia in the quantitative determination of halogens in organic compounds was first suggested by Dr. H. P. Cady of this University. The idea has since received the further attention and study of Dr. F. B. Daine of the Department of Organic Chemistry, under whose direction research was done upon the subject by T. H. Vaughn.[1] A French chemist, Chablay, published in 1913 a book "On the use of the Metal Ammonium Compounds in Organic Chemistry" in which he has given the results of a considerable number of determinations on various organic halogen compounds.

The general method as described and used by Chablay and Vaughn[1] consists in dissolving the sample in about 30 c.c. L. A. drawn into a Dewar Test Tube. To this solution small pieces of clean metallic sodium are added until the blue coloration which results is permanent. This is allowed to stand for one hour, when pure ammonium nitrate is slowly added to take up the excess sodium. The solution is evaporated to dryness and the residue dissolved

(1) T. H. Vaughn, Thesis, 1916.

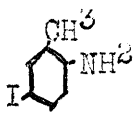
in a small amount of water. The water solution is made acid with dilute nitric acid and titrated with silver nitrate and ammonium thiocyanate, using a nitric acid solution of ferric alum as an indicator. The ferric alum is saturated and made acid with nitric acid until the red color disappears. Five c.c. of the indicator are used for each titration.

Chablay's published results cover chlorine, bromine and iodine compounds. Vaughn has limited his to chlorine and bromine compounds, stating that iodine compounds cannot be determined by this method directly. He further mentions having attempted determinations on compounds containing more than one of the halogens, but without success.

In this work special attention has been given to those organic compounds which contain iodine, many of which also contained either chlorine or bromine. One compound containing three halogens was attempted, but the results did not indicate successful determinations. Most of the compounds on which determinations have been made were prepared by the method with nitric acid as described in Part I.

GENERAL DISCUSSION OF METHOD.

The principal difficulty encountered in this work was the element of uncertainty in the final titration due to excess color in the solution. This color does not alone seem to be due to the presence of iodine, but rather to depend upon the complexity of the structure of the compound. It appeared to be more evident in those containing nitrogen. The following titration is illustrative of results from such a compound.

Determination of iodine in 

Sample No.	I.		II.	
	.0835		.2531	
	$AgNO_3$	NH_4NCS	$AgNO_3$	NH_4NCS
C.C.	10.00	2.90	25.05	4.75
Difference	7.10		20.30	

Calculations.

No. I. $\frac{7.10 \times .006346}{.0835}$ = 53.96 p'cnt.

II. $\frac{20.30 \times .006346}{.2531}$ = 50.90 "

Theoretical iodine content = 54.49 "

The most natural and effective way in which

to deal with the excessive color was found to be filtration. This filtration was best carried out after precipitation of the halide by silver nitrate. This, when heated, coagulates and thus carries out with it most of the coloring matter. The filtrate is left fairly clear and colorless. The residue must be thoroly washed with warm water.

It was noted from the determination recorded on the previous page that the larger sample was more highly colored. For this reason the size of samples used was cut down to .05 -.08 grams.

Excessive acidification also causes excessive color. The point at which the solution becomes acid is usually indicated by a change to a yellow tinge. This deepend to a reddish color is more acid is added.

The amount of sodium to be used is, of course, in excess of the theoretical amount required. But the absence of blue color does not indicate insufficient sodium, for the mixture may be made to lose its color after a few minutes vigorous stirring even after quite large amounts of sodium have already been added. This is due to the formation of the white sodamide. The amount of sodium ordin-

arily used in the most successful titrations was .2 - .3 grams. This was added in about .05 - .75 gram portions with vigourous stirring at intervals. That this stirring is important for a successful determination is indicated by a comparison of the following experiment in which all the above mentioned precautions were used,

Samples of 2-amido 5-iodo-toluene

Sample No.	No. I.		No. II.	
grams	.0596		.0711	
	$AgNO^3$	NH^4NCS	$AgNO^3$	NH^4NCS
c.c.	7.15	2.05	5.75	1.65
Difference	5.10		6.10	

Calculations.		Percent
No. I.	$\frac{5.10 \times .006346}{.0596}$	54.32
II.	$\frac{6.10 \times .006346}{.0711}$	54.47
Theoretical iodine content		54.49

with the one given just below in which .7 gram sodium was placed in the L.A. and allowed to stand until evaporation had taken place without further agitation.

Samples of 2-amido 5-iodo-toluene

Sample No.	I.	II.
grams	.0979	.0995

	$AgNO_3$	NH_4NCS	$AgNO_3$	NH_4NCS
c.c.	20.70	8.80	37.75	14.65
Difference	11.90		13.10	

Calculations. Percent.

No. I $\frac{11.90 \times .003173}{.0979}$ 38.58

II. $\frac{13.10 \times .003173}{.0995}$ 41.79

Theoretical iodine content 54.49

The use of absolute alcohol and also ammonium nitrate for the purpose of taking up any excess sodium that might be present, was mentioned by Chablay. Both were tried in the course of these experiments, but their use was finally abandoned. This was done, in the first place, because it was thot that, in some cases at least, the coloring of the solution was deepened by the addition of these substances. Then also, it was evident that the chances for a more perfect reaction between the sodium and halide would be increased if they were permitted to be in contact during the several hours required for complete evaporation of the ammonia. In no case did a violent reaction take place upon the addition of water to the residue.

The small size of the samples used increased

the liability to error in titration, and for that reason N/40 reagents were resorted to instead of the N/20 used by Chablay and Vaughn.

The method by which the greatest number of successful determination were carried out is here given in detail.

For solids, .05 - .08 gm. samples were weighed into each of two Dewar tubes. The liquid-ammonia, having been drawn into a separate Dewar tube, was transferred under its own pressure by siphon to the tubes containing the samples. This was done cautiously so as to avoid excessive boiling and possible loss of sample. Clean metallic sodium, .2 - .3 gm. was added in small portions with vigorous stirring after each addition. All the sodium having been stirred in, the samples were set aside and the ammonia allowed to evaporate. The residue, consisting of sodium halide, sodamide and the breaking-down products of the organic compound, was then dissolved in 20 - 30 c.c. of lukewarm water and washed into beakers. It was made just acid with dilute nitric acid and N/40 silver nitrate added in amounts 2 - 8 c.c. in excess of the calculated possible amount that might be required. Heat was applied just to the point of boiling

and the mixture filtered, beakers and residue being carefully washed with warm water. The filtrate was cooled to room temperature and a measured amount of silver nitrate added to insure the presence of an excess. Five c.c. of the ferric alum indicator were then added and the titration carried to a distinct red color with N/40 ammonium thiocyanate. The red color was then discharged with more silver nitrate and the point of change noted. The titration may be carried back and forth as often as necessary to catch a good end-point without affecting the results.

For liquids, special glass-stoppered capsules were prepared in which the sample could be weighed and then placed directly into the liquid-ammonia. The titration was carried on exactly as above.

On the pages following there will be found a detailed record of the determinations carried out by the above method. In each case a few notations are added as to the particular conditions.

I. Determination of iodine in 2-amido 5-iodo-toluene, using N/20 $AgNO^3$, absolute alcohol and filtering while cold. End point obscured by color.

Sample No.	I		II.	
Grams	.0833		.1249	
	$AgNO^3$	$NH4NCS$	$AgNO^3$	NH^4NCS
c.c.	7.90	.90	13.85	2.50
Difference	7.00		10.35	

Sample No.	III.		IV.	
Grams	.0540		.0527	
c.c.	7.05	2.25	7.05	2.40
Difference	4.80		4.65	

Calculations.

		Percent.
No. I.	$\frac{7.00 \times .006346}{.0833}$	53.32
II.	$\frac{10.35 \times .006346}{.1249}$	52.60
III.	$\frac{4.80 \times .006346}{.0540}$	56.40
IV.	$\frac{4.65 \times .006346}{.0527}$	56.00

Theoretical iodine content 54.49

II. Determination of bromine in para-di-brom-benzene, using N/20 reagents.

Sample No.	I.		II.	
Grams	.1151		.1088	
	$AgNO^3$	NH^4NCS	$AgNO^3$	NH^4NCS
c.c.	21.65	1.90	20.20	1.60
Difference	19.75		18.60	

Calculations.		Percent.
No. I.	$\frac{19.75 \times .003996}{.1151}$	68.58
II.	$\frac{18.60 \times .003996}{.1088}$	67.96
Theoretical bromine content		67.77

III. Determination of iodine in iodoform, using N/40 reagents.

Sample No.	I.		II.	
Grams	.0774		.0800	
	$AgNO^3$	NH^4NCS	$AgNO^3$	NH^4NCS
c.c.	25.65	2.00	31.85	7.70
Difference	23.65		24.15	

Sample No.	III.	
Grams	.1041	
c.c.	36.75	5.25
Difference	31.50	

Calculations. (Iodoform)		Percent
No. I.	$\frac{23.65 \times .003173}{.0774}$	96.95
II.	$\frac{24.15 \times .003173}{.0800}$	95.80
III.	$\frac{31.5 \times .003173}{.1041}$	96.01
Theoretical iodine content		96.69

IV. Determination of iodine in sample prepared by W. M. Janney. Suspected iodine content 51.00 percent.

Sample No.	I.		II.	
Grams	.0500		.0632	
	$AgNO^3$	NH^4NCS	$AgNO^3$	NH^4NCS
c.c.	35.10	26.00	35.10	24.10
Difference	9.10		11.00	

Calculations		Percent.
No. I.	$\frac{9.10 \times .003173}{.0500}$	57.75
II.	$\frac{11.00 \times .003173}{.0632}$	55.23

V. Determination of iodine and chlorine in para-chlor-iod-benzene, using N/40 reagents. Nothing used to take up the excess sodium. Filtered and washed while hot.

Sample No.	I.		II.	
Grams	.0751		.1119	
	$AgNO_3$	NH_4NCS	$AgNO_3$	NH_4NCS
c.c.	35.00	10.00	40.00	2.60
Difference	25.00		37.40	

Calculations for iodine (para-chlor-iod-benzene)

		Percent.
No. I.	$\frac{12.50 \times .003173}{.0751}$	52.85
II.	$\frac{18.70 \times .003173}{.1119}$	52.95
Theoretical iodine content		53.20

Calculations for chlorine.

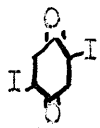
No. I.	$\frac{12.50 \times .0008865}{.0751}$	14.75
II.	$\frac{18.70 \times .0008865}{.1119}$	14.80
Theoretical chlorine content		14.88

VI. Determination of iodine in para-iod-anisole. N/40 reagents used. Nothing to take up excess Na. Filtered while hot.

Sample No.	I.	
Grams	.0796	
	$AgNO_3$	NH_4NCS
c.c.	16.95	3.50
Difference	13.45	

Calculations (Para-Iod-anisole)		Percent
No. I.	$\frac{13.45 \times .003173}{.0796}$	53.62
Theoretical iodine content		54.25

VII. Determination of iodine in the unidentified product melting at 130° which was obtained from acetanilide at 113° by the nitric acid method. (P. 23)

Thot to be  Method the same as above.

Sample No.	I.		II.	
Grams.	.0395		.0432	
	$AgNO_3$	NH_4NCS	$AgNO_3$	NH_4NCS
c.c.	15.55	6.75	15.00	5.25
Difference	8.80		9.75	

Calculations.		Percent.
No. I.	$\frac{8.80 \times .003173}{.0395}$	70.53
II.	$\frac{9.75 \times .003173}{}$	69.99
Theoretical, if as above indicated,		70.00

VIII. Determination of iodine in para-iod-nitro-benzene.  Method as above.

Sample No.	I.		II.	
Grams	.0808		.0764	
	$AgNO^3$	NH^4NCS	$AgNO^3$	NH^4NCS
c.c.	19.13	6.15	18.55	6.55
Difference	13.00		12.00	

Calculations (Para-iod-nitro-benzene) Percent

No. I. $\frac{13.00 \times .003173}{.0808}$ 51.05

II. $\frac{12.00 \times .003173}{.0764}$ 49.85

Theoretical iodine content 50.98

IX. Determination of iodine in para-iod-acetanilide.

I

Samples No.	I.		II.	
Grams	.0605		.0632	
	$AgNO^3$	NH^4NCS	$AgNO^3$	NH^4NCS
c.c.	12.00	2.25	12.00	2.35
Difference	9.25		9.65	

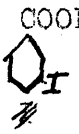
Calculations Percent

No. I. $\frac{9.25 \times .003173}{.0605}$ 48.65

II. $\frac{9.65 \times .003173}{.0632}$ 48.38

Theoretical iodine content 48.83

X. Determination of iodine in ~~para~~ meta-iod-benzoic acid.



Sample No.	I.		II.	
Grams	.0672		.1157	
	$AgNO^3$	NH^4NCS	$AgNO^3$	NH^4NCS
c.c.	12.20	1.35	20.00	1.40
Difference	10.85		18.60	

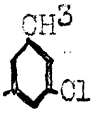
Calculations. Percent.

No. I. $\frac{10.85 \times .003173}{.0672}$ 51.23

II. $\frac{10.60 \times .003173}{}$ 51.01

Theoretical iodine content 51.19

XI. Determination of iodine in meta-chlor-iod-toluene.

? (I) 

(1) Liquid boiling at 230°- 250°.

Samples No.	I.		II.	
Grams	.0891		.0832	
	AgNO3	NH^4NCS	$AgNO^3$	NH^4NCS
c.c.	29.85	6.50	31.35	9.80
Difference	23.35		21.55	

	III.	
Grams	.0719	
c.c.	20.00	2.60

Sample No.	III.	
Grams	.0719	
	$AgNO^3$	NH^4NCS
c.c.	30.00	2.60
Difference	17.40	

Calculations.

		Percent.
No. I.	$\frac{11.68 \times .003173}{.0719}$	41.60
II.	$\frac{1028 \times .003173}{.0832}$	39.30
III.	$\frac{8.70 \times .003173}{.0719}$	38.30
Theoretical		50.28

(2) On the redistilled oil boiling at 241° - 243°.

Sample No.	I.		II.	
Grams	.0664		.0657	
	AgNO3	NH4NCS	AgNO3	NH4NCS
c.c.	22.40	2.70	21.60	1.95
Difference	19.70		19.65	

Calculations.

		Percent.
No. I.	$\frac{9.85 \times .003173}{.0664}$	47.07
II.	$\frac{9.82 \times .003173}{.0657}$	47.40
Theoretical iodine content		50.28

(3) Second preparation of meta-chlor-iod-toluene, boiling at 242° - 243°.

Sample No.	I.		II.	
Grams	.0619		.0703	
	$AgNO_3$	NH_4NCS	$AgNO_3$	NH_4NCS
c.c.	23.00	3.65	23.00	1.10
Difference	19.45		21.90	

Calculations for iodine. Percent.

No. I. $\frac{9.72 \times .003173}{.0619}$ 49.80

II. $\frac{10.95 \times .003173}{.0703}$ 49.40

Theoretical iodine content 50.28

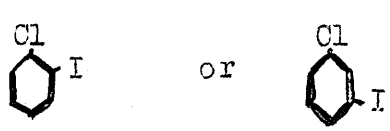
Calculations for chlorine.

No. I. $\frac{9.72 \times .008865}{.0619}$ 13.92

II. $\frac{10.95 \times .008865}{.0703}$ 13.81

Theoretical chlorine content 14.08

XII. Determination of iodine and chlorine in



Sample No.	I.		II.	
Grams	.0688		.0683	
	$AgNO^3$	NH_4NCS	$AgNO^3$	NH_4NCS
c.c.	27.45	4.55	25.45	2.65
Difference	22.90		22.80	

Calculations for iodine. Percent.

No. I. $\frac{11.45 \times .003173}{.0688}$ 52.80

II. $\frac{11.40 \times .003173}{.0683}$ 53.00

Theoretical iodine content 53.20

Calculations for chlorine.

No. I. $\frac{11.45 \times .0008865}{.0688}$ 14.75

II. $\frac{11.40 \times .0008865}{.0683}$ 14.80

Theoretical chlorine content 14.88

XIII. Determination of bromine and chlorine in para-brom-iod-benzene.

Sample No.	I.	II.
Grams	.0650	.0844

	$AgNO_3$	NH_4NCS	$AgNO_3$	NH_4NCS
c.c.	21.40	3.10	29.35	5.15
Difference	18.30		24.40	

Calculations for iodine. Percent.

No. I. $\frac{9.15 \times .003173}{.0650}$ 44.67

II. $\frac{12.20 \times .003173}{.0844}$ 45.85

Theoretical iodine content 44.85

Calculations for bromine.

No. I. $\frac{9.15 \times .001998}{.0650}$ 28.13

II. $\frac{12.20 \times .001998}{.0844}$ 28.88

Theoretical bromine content 28.26

XIV. Determination of iodine and chlorine in ortho-chlor-iod-toluene.

(?)

(1) Undistilled portion.

Sample No.	I.		II.	
Grams	.0609		.0659	
	$AgNO_3$	NH_4NCS	$AgNO_3$	NH_4NCS
c.c.	23.30	7.35	24.05	7.30
Difference	15.90		16.70	

Calculations (ortho-chlor-iod-toluene) Percent.

No. I. $\frac{7.95 \times .003173}{.0609}$ 41.47

II. $\frac{8.35 \times .003173}{.0659}$ 40.21

Theoretical iodine content. 50.20

(2) Solidified portion which boiled over at 190° - 218° under 52 mm. pressure.

Sample No.	I.		II.	
Grams	.0603		.0600	
	$AgNO_3$	NH_4NCS	$AgNO_3$	NH_4NCS
c.c.	20.70	2.15	21.35	3.50
Difference	18.55		17.85	

Calculations Percent.

No. I. $\frac{9.30 \times .003173}{.0603}$ 48.94

II. $\frac{8.95 \times .003173}{.0600}$ 47.35

Theoretical iodine content 50.20

(3) On solidified portion of ortho-chlor-iod-toluene boiling over at 215°-220° under 52 mm. and melting at 72° - 74°.

Sample No.	I.		II.	
Grams	.0630		.0891	
	$AgNO_3$	NH_4NCS	$AgNO_3$	NH_4NCS
c.c.	24.10	3.95	32.00	3.75
Difference	20.15		28.25	

Calculations for iodine . Percent.

No. I. $\frac{10.05 \times .003173}{.0630}$ 50.62

II. $\frac{14.10 \times .003173}{.0891}$ 50.21

Theoretical iodine content 50.20

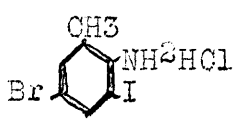
Calculations for chlorine

No. I. $\frac{10.05 \times .0008865}{.0630}$ 14.14

II. $\frac{14.10 \times .0008865}{.0891}$ 14.03

Theoretical chlorine content 14.08

XV. Determination of iodine, chlorine and bromine in (2)iod-(5)brom-toluidine-hydrochloride .



(This, the only compound tried containing three halogens, was prepared by A. T. Beckly.)

Sample No.	I.		II.	
Grams	.0788		.0989	
	$AgNO_3$	NH_4NCS	$AgNO_3$	NH_4NCS
c.c.	24.70	5.70	31.15	6.90
Difference	19.00		24.25	
Sample No.	III.		IV.	
Grams	.0501		.0587	
c.c.	20.40	4.95	22.25	4.35
Difference	15.45		17.90	

Calculations for chlorine.		Percent.
No. I.	$\frac{6.35 \times .0008865}{.0788}$	7.14
II.	$\frac{8.10 \times .0008865}{.0989}$	7.28
III.	$\frac{5.15 \times .0008865}{.0501}$	9.11
IV.	$\frac{5.95 \times .0008865}{.0587}$	8.99
Theoretical chlorine content		10.19

(Calculations for bromine and iodine would prove proportionately below theoretical percentage.)